

补充材料

(111)取向无铅 $K_{0.5}Na_{0.5}NbO_3$ 外延薄膜的相变和电卡效应：外应力与错配应变效应白刚^{1)†} 韩宇航¹⁾ 高存法²⁾

1)(南京邮电大学集成电路科学与工程学院,南京 210026)

2)(南京航空航天大学机械结构力学及控制国家重点实验室,南京 210016)

为了探索(111)取向 $K_{0.5}Na_{0.5}NbO_3$ 铁电薄膜中的相变和电卡效应,首先建立了基于八阶朗道自由能的(111)取向铁电薄膜非线性热力学理论。钙钛矿块状铁电晶体的标准弹性吉布斯能量函数 G 由下式给出:

$$\begin{aligned}
G = & \alpha_1 (p_1^2 + p_2^2 + p_3^2) + \alpha_{11} (p_1^4 + p_2^4 + p_3^4) + \alpha_{12} (p_1^2 p_2^2 + p_1^2 p_3^2 + p_2^2 p_3^2) + \alpha_{111} (p_1^6 + p_2^6 + p_3^6) \\
& + \alpha_{112} [p_1^4 (p_2^2 + p_3^2) + p_2^4 (p_1^2 + p_3^2) + p_3^4 (p_2^2 + p_1^2)] + \alpha_{123} p_1^2 p_2^2 p_3^2 + \alpha_{1111} (p_1^8 + p_2^8 + p_3^8) \\
& + \alpha_{1112} [p_1^6 (p_2^2 + p_3^2) + p_2^6 (p_1^2 + p_3^2) + p_3^6 (p_2^2 + p_1^2)] + \alpha_{1122} (p_1^4 p_2^4 + p_1^4 p_3^4 + p_2^4 p_3^4) + \\
& \alpha_{1123} (p_1^4 p_2^2 p_3^2 + p_1^2 p_2^4 p_3^2 + p_1^2 p_2^2 p_3^4) - \frac{1}{2} s_{11} (\tilde{\sigma}_1^2 + \tilde{\sigma}_2^2 + \tilde{\sigma}_3^2) - s_{12} (\tilde{\sigma}_1 \tilde{\sigma}_2 + \tilde{\sigma}_1 \tilde{\sigma}_3 + \tilde{\sigma}_2 \tilde{\sigma}_3) \\
& - \frac{1}{2} s_{44} (\tilde{\sigma}_4^2 + \tilde{\sigma}_5^2 + \tilde{\sigma}_6^2) - Q_{11} (\tilde{\sigma}_1 p_1^2 + \tilde{\sigma}_2 p_2^2 + \tilde{\sigma}_3 p_3^2) - Q_{44} (\tilde{\sigma}_4 p_2 p_3 + \tilde{\sigma}_5 p_1 p_3 + \tilde{\sigma}_6 p_1 p_2) \\
& - Q_{12} [\tilde{\sigma}_1 (p_2^2 + p_3^2) + \tilde{\sigma}_2 (p_1^2 + p_3^2) + \tilde{\sigma}_3 (p_2^2 + p_1^2)],
\end{aligned} \tag{S1}$$

其中 p_i 和 $\tilde{\sigma}_i$ 晶体参考系 $x(x_1, x_2, x_3)$ (x_1, x_2, x_3 分别对应于立方晶胞的 [100], [010]和[001]晶轴) 中的极化矢量和应力张量的分量。在 (S1) 式中, $\alpha_i, \alpha_{ij}, \alpha_{ijk}$ 和 α_{ijkl} 是介电刚度系数; s_{ij} 代表弹性柔量; Q_{ij} 是电致伸缩系数。这些材料参数列于表 S1。

为了得到(111)取向铁电外延薄膜的热力学势,必须知道不同参考系下极化矢量与应力张量的关系。可以使用矩阵 t_{ij} 来描述晶体参考系 $x(x_1, x_2, x_3)$ 和全局坐标系 $X(X_1, X_2, X_3)$ 其中 X_1, X_2, X_3 分别对应伪立方晶胞的 $[1\bar{1}0], [11\bar{2}]$ 和 $[111]$ 晶向:

$$t_{ij} = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & -\frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{bmatrix}. \tag{S2}$$

通过矩阵变换得到 $p = (t_{ij})^{-1} P$ 和 $\tilde{\sigma} = (t_{ij})^{-1} \sigma t_{ij}$, 其中 p 和 P 分别是晶体参考系 x 和薄膜参考系 X 中的极化矢量, $\tilde{\sigma}$ 和 σ 分别是参考系 x 和 X 中的应力

张量矩阵。

对于(111)取向外延薄膜，面内失配应变为 u_1, u_2 和 u_6 (全局坐标下)，薄膜的热力学势 G_f 可以通过勒让德变换得到：

$$G_f = G + u_1\sigma_1 + u_2\sigma_2 + u_6\sigma_6. \quad (\text{S3})$$

当面内双轴应变为等方双轴应变且切应变为零时，薄膜在垂直于薄膜方向受到一个外应力，那么薄膜受到混合机械边界条件为

$$u_1 = u_2 = u_m, \quad u_6 = 0, \quad \sigma_3 \neq 0, \quad \sigma_4 = \sigma_5 = 0, \quad u_i = -\partial G / \partial \sigma_i, \quad (\text{S4})$$

根据(S4)式求出应力表达式，然后代入(S3)式中，得到(111)取向薄膜的自由能 G_f 的表达式为

$$G_f = a_1^*(P_1^2 + P_2^2) + a_3^*P_3^2 + a_{11}^*(P_1^2 + P_2^2)^2 + a_{33}^*P_3^4 + a_{13}^*P_3^2(P_1^2 + P_2^2) + a_{2223}P_2P_3(P_2^2 - 3P_1^2) + G^{(6)} + G^{(8)} + \frac{3(4u_m + s_{44}\sigma_3)^2}{8(4s_{11} + 8s_{12} + s_{44})} - \frac{8u_m + 3s_{44}\sigma_3}{8}\sigma_3, \quad (\text{S5})$$

$$a_1^* = a_1 - \frac{4Q_{11} + 8Q_{12} + Q_{44}}{4s_{11} + 8s_{12} + s_{44}}u_m - \frac{s_{44}(Q_{11} + 2Q_{12}) - Q_{44}(s_{11} + 2s_{12})}{4s_{11} + 8s_{12} + s_{44}}\sigma_3, \quad (\text{S6})$$

$$a_3^* = a_1 - \frac{4Q_{11} + 8Q_{12} - 2Q_{44}}{4s_{11} + 8s_{12} + s_{44}}u_m - \frac{s_{44}(Q_{11} + 2Q_{12}) + 2Q_{44}(s_{11} + 2s_{12})}{4s_{11} + 8s_{12} + s_{44}}\sigma_3, \quad (\text{S7})$$

$$a_{11}^* = \frac{1}{4}(2a_{11} + a_{12}) + \frac{1}{24} \left[\frac{(4Q_{11} + 8Q_{12} + Q_{44})^2}{4s_{11} + 8s_{12} + s_{44}} + \frac{2(Q_{11} - Q_{12} + Q_{44})^2}{s_{11} - s_{12} + s_{44}} \right], \quad (\text{S8})$$

$$a_{33}^* = \frac{1}{3}(a_{11} + a_{12}) + \frac{(2Q_{11} + 4Q_{12} - Q_{44})^2}{6(4s_{11} + 8s_{12} + s_{44})}, \quad (\text{S9})$$

$$a_{13}^* = 2a_{11} + \frac{1}{6} \left[\frac{(2Q_{11} + 4Q_{12} - Q_{44})(4Q_{11} + 8Q_{12} + Q_{44})}{4s_{11} + 8s_{12} + s_{44}} + \frac{(2Q_{11} - 2Q_{12} - Q_{44})^2}{s_{11} - s_{12} + s_{44}} \right], \quad (\text{S10})$$

$$a_{2223} = \frac{\sqrt{2}}{3}(a_{12} - 2a_{11}) + \frac{(Q_{11} - Q_{12} + Q_{44})(-2Q_{11} + 2Q_{12} + Q_{44})}{3\sqrt{2}(s_{11} - s_{12} + s_{44})}, \quad (\text{S11})$$

$$G^{(6)} = a_{111} \left[\left(-\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^6 + \left(\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^6 + \left(\frac{\sqrt{3}}{3}P_3 - \frac{\sqrt{6}}{3}P_2\right)^6 \right] + a_{112} \left\{ \left[\left(-\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^4 + \left(\frac{\sqrt{3}}{3}P_3 - \frac{\sqrt{6}}{3}P_2\right)^4 \right] \left(\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^2 \right. \\ + \left[\left(\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^4 + \left(\frac{\sqrt{3}}{3}P_3 - \frac{\sqrt{6}}{3}P_2\right)^4 \right] \left(-\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^2 \\ \left. + \left(\frac{\sqrt{3}}{3}P_3 - \frac{\sqrt{6}}{3}P_2\right)^2 \left[\left(-\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^4 + \left(\frac{\sqrt{2}}{2}P_1 + \frac{\sqrt{6}}{6}P_2 + \frac{\sqrt{3}}{3}P_3\right)^4 \right] \right\} + \frac{a_{123}}{108}(P_3 - \sqrt{2}P_2)^2(-3P_1^2 + P_2^2 + 2\sqrt{2}P_2P_3 + 2P_3^2)^2, \quad (\text{S12})$$

$$\begin{aligned}
G^{(8)} = & a_{1111} \left[\left(\frac{\sqrt{3}}{3} P_3 - \frac{\sqrt{6}}{3} P_2 \right)^8 + \left(\frac{\sqrt{3}}{3} P_3 - \frac{\sqrt{2}}{2} P_1 + \frac{\sqrt{6}}{6} P_2 \right)^8 + \left(\frac{\sqrt{3}}{3} P_3 + \frac{\sqrt{2}}{2} P_1 + \frac{\sqrt{6}}{6} P_2 \right)^8 \right] \\
& + \frac{a_{1122}}{1679616} \left\{ (-3\sqrt{2}P_1 + \sqrt{6}P_2 + 2\sqrt{3}P_3)^4 (3\sqrt{2}P_1 + \sqrt{6}P_2 + 2\sqrt{3}P_3)^4 \right. \\
& + 144(P_3 - \sqrt{2}P_2)^4 [(-3\sqrt{2}P_1 + \sqrt{6}P_2 + 2\sqrt{3}P_3)^4 + (3\sqrt{2}P_1 + \sqrt{6}P_2 + 2\sqrt{3}P_3)^4] \left. \right\} \\
& + a_{1112} \left\{ \frac{1}{81} (P_3 - \sqrt{2}P_2)^6 (3P_1^2 + P_2^2 + 2P_3^2 + 2\sqrt{2}P_2P_3) \right. \\
& + \left[\frac{1}{3} (P_3 - \sqrt{2}P_2)^2 + \left(-\frac{\sqrt{2}}{2} P_1 + \frac{\sqrt{6}}{6} P_2 + \frac{\sqrt{3}}{3} P_3 \right)^2 \right] \left(\frac{\sqrt{2}}{2} P_1 + \frac{\sqrt{6}}{6} P_2 + \frac{\sqrt{3}}{3} P_3 \right)^6 \\
& + \left[\frac{1}{3} (P_3 - \sqrt{2}P_2)^2 + \left(\frac{\sqrt{2}}{2} P_1 + \frac{\sqrt{6}}{6} P_2 + \frac{\sqrt{3}}{3} P_3 \right)^2 \right] \left(-\frac{\sqrt{2}}{2} P_1 + \frac{\sqrt{6}}{6} P_2 + \frac{\sqrt{3}}{3} P_3 \right)^6 \left. \right\} \\
& + \frac{a_{1123}}{3888} (P_1^2 + P_2^2 + P_3^2) (P_3 - \sqrt{2}P_2)^2 (-3\sqrt{2}P_1 + \sqrt{6}P_2 + 2\sqrt{3}P_3)^2 (3\sqrt{2}P_1 + \sqrt{6}P_2 + 2\sqrt{3}P_3)^2.
\end{aligned} \tag{S13}$$

极化平衡态可通过自由能 G_f 对极化 P_i 求极小值获得。介电常数可由方程 $\epsilon_0 \epsilon_{ij} = \epsilon_0 + \eta_{ij}$ (ϵ_0 为真空介电常数, η_{ij} 为介电极化率) 获得。首先导出了介电极化率的倒数即介电刚度 $\eta_{ij}^{-1} = \partial^2 G_f / \partial P_i \partial P_j$ 的表达式, 然后应用矩阵求逆得到介电常数, 再根据 $d_{ij} = b_{kj} \eta_{ki}$ 计算压电系数 d_{ij} , 其中 $b_{kj} = \partial u_j / \partial P_k$ 。

表 S1 $K_{0.5}Na_{0.5}NbO_3$ 的材料参数

Table S1. Parameters for $K_{0.5}Na_{0.5}NbO_3$, where T is the temperature in K.

Parameters	Values	Units	References
α_1	$4.29 \times 10^7 \times [\text{Coth}(140/T) - \text{Coth}(140/657)]$	$C^{-2} m^2 N$	[S1]
α_{11}	-2.7302×10^8	$C^{-4} m^6 N$	[S1]
α_{12}	1.0861×10^9	$C^{-4} m^6 N$	[S1]
α_{111}	3.0448×10^9	$C^{-6} m^{10} N$	[S1]
α_{112}	-2.7270×10^9	$C^{-6} m^{10} N$	[S1]
α_{123}	1.5513×10^{10}	$C^{-6} m^{10} N$	[S1]
α_{1111}	2.4044×10^{10}	$C^{-8} m^{14} N$	[S1]
α_{1112}	3.7328×10^9	$C^{-8} m^{14} N$	[S1]
α_{1122}	3.3485×10^{10}	$C^{-8} m^{14} N$	[S1]
α_{1123}	-6.2017×10^{10}	$C^{-8} m^{14} N$	[S1]
Q_{11}	0.16	$C^{-2} m^4$	[S1]
Q_{12}	-0.072	$C^{-2} m^4$	[S1]
Q_{44}	0.084	$C^{-2} m^4$	[S1]
s_{11}	5.57×10^{-12}	m^2/N	[S1]
s_{12}	-1.57×10^{-12}	m^2/N	[S1]
s_{44}	13.1×10^{-12}	m^2/N	[S1]
ρ	4514	kg/m^3	[S2]
c_p	200	$J/(kg K)$	[S2]

表 S2 (111)取向 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ 薄膜中可能出现的相结构

Table S2. Equilibrium phase structures appearing in (111) oriented $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ferroelectric thin film.

相	全局坐标系(X)	晶体坐标系(x)
顺电相 PE	$P_1=P_2=P_3=0$	$p_1=p_2=p_3=0$
三方相 R	$P_1=P_2=0, P_3\neq 0$	$p_1=p_2=p_3\neq 0$
单斜相 M	$P_1=0, P_2\neq 0, P_3\neq 0$	$p_1=p_2\neq 0, p_3\neq 0$
正交相 O	$P_1\neq 0, P_2=P_3=0$	$p_1=p_2\neq 0, p_3=0$

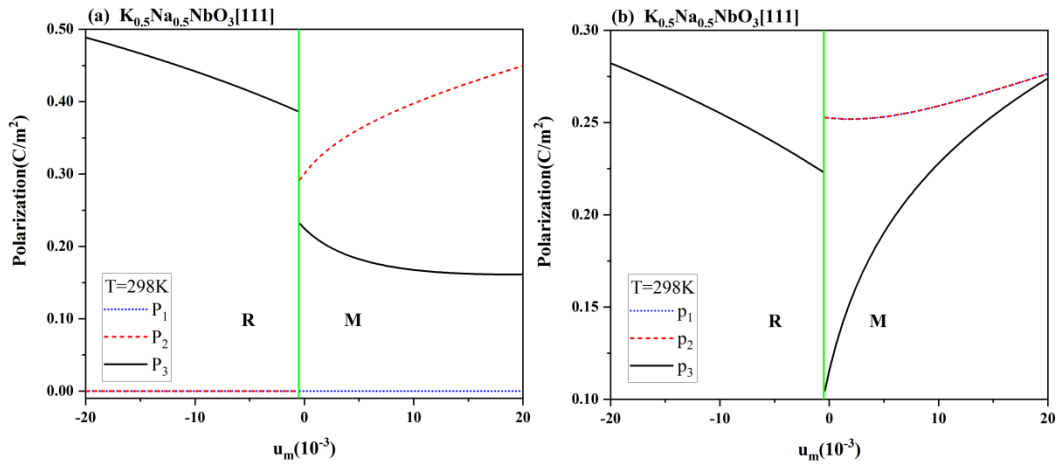


图 S1 室温 $T = 298 \text{ K}$ 下, (a) 全局坐标系和 (b) 晶体坐标系中极化分量与失配应变的关系

Fig. S1. Polarization components as a function of misfit strain at room temperature $T = 298 \text{ K}$ in (a) global coordinate system and (b) crystal coordinate system, respectively.

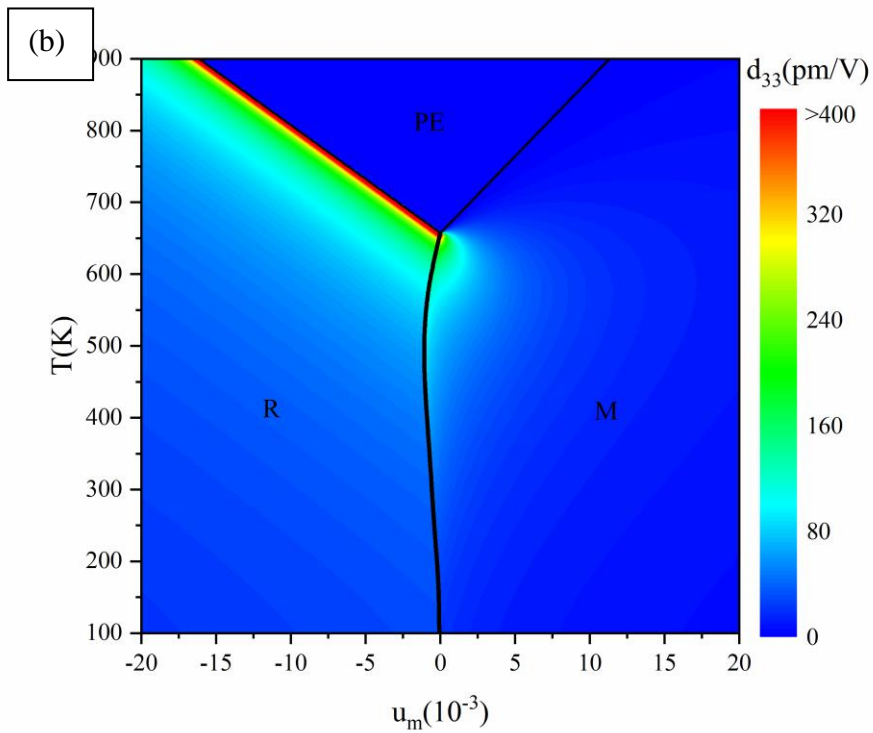
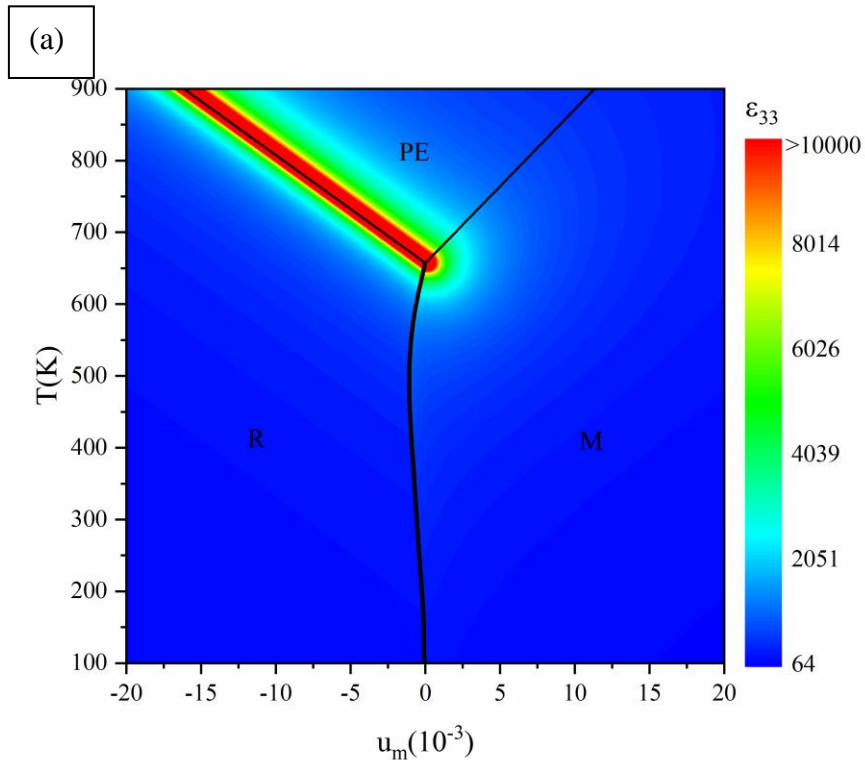
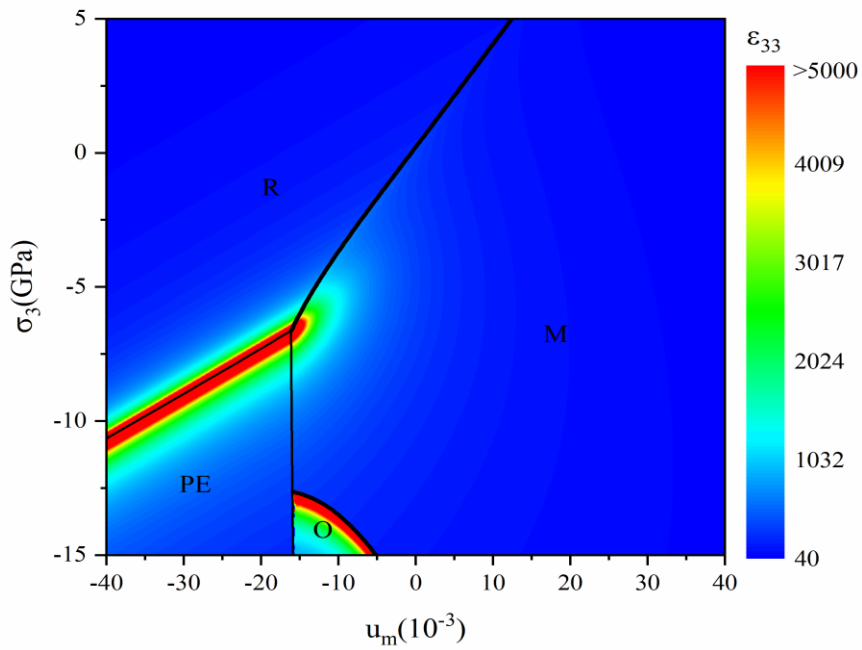


图 S2 无外部电场和外部应力下, (a)面外介电和 (b) 面外压电特性随温度和失配应变的分布

Fig. S2. Distribution of (a) the out-of-plane dielectric and (b) the out-of-plane piezoelectric properties with temperature and misfit strain without the external electric field without the external stress.

(a)



(b)

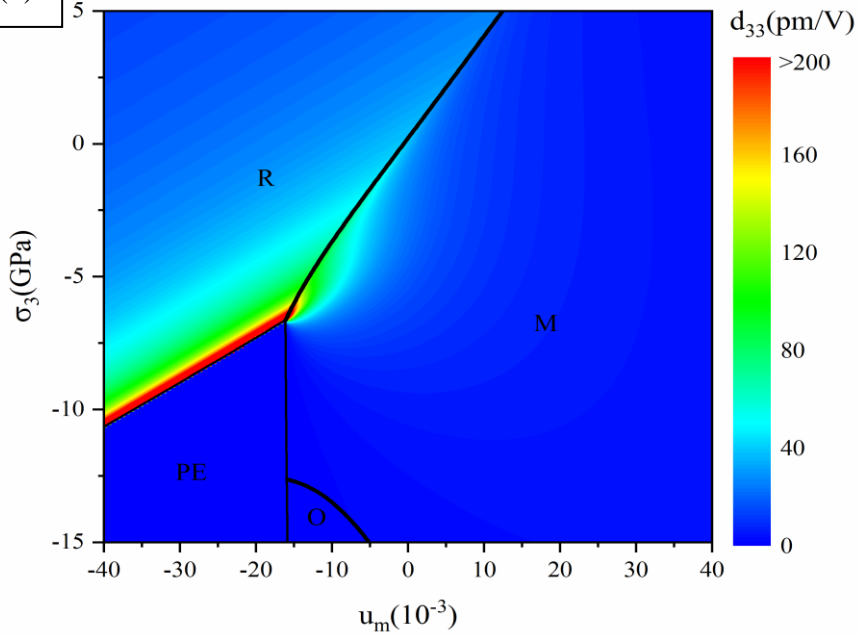


图 S3 室温下无外部电场时，(a)面外介电和(b)面外压电特性随外部应力和失配应变的分布

Fig. S3. Distribution of (a) the out-of-plane dielectric and (b) the out-of-plane piezoelectric properties with a wide range of external stress and misfit strain without the external electric field under room temperature ($T = 298$ K).

参考文献

[S1]Pohlmann H, Wang J, Wang B, Chen L 2017 *Appl. Phys. Lett.* **110** 102906.

[S2]Li C, Huang Y, Wang J, et al. 2021 *Npj Comput. Mater.* **7** 1.